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| (54) Title: ANISOTROPIC CONDUCTIVE ADHESIVE FILM (57) Abstract A composition for forming an anisotropic conductive film having a rapid curing speed, high heat resistance, high humidity resistance, long shelf life and excellent repairability comprising an adhesive composition containing about 100 parts cyanate ester, from about 0.01 part to 10 parts of a curing catalyst, from about 10 parts to about 300 parts of a film-formable thermoplastic resin, and from about 10 to about 500 parts of an epoxy resin, and from about 0.1 part to about 20 parts conductive particles per 100 parts total adhesive composition. | | |

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ANISOTROPIC CONDUCTIVE ADHESIVE FILMBackground of the Invention5 Field of the Invention

The present invention relates to an anisotropic adhesive composition, and Z-axis adhesive film formed therefrom.

10 Description of the Related Art

Recently, with the development of high-density mounting and improved techniques in making electrical components, electrical circuits have become smaller and have higher connection densities. For bonding these
15 precise and fine-pitch circuits, conductive adhesives have been frequently used. Ideally, a conductive adhesive is provided as a self-supporting film. Liquid systems, such as prior art epoxies will migrate due to capillary action and may touch or contaminate a critical
20 area of the circuit. Anisotropic conductive films, also known as Z-axis films have been proposed. One advantage is that ZAFs provide pressure-engaged connections. Therefore, excellent resistance stability, high peel adhesion, and high insulative resistivity are needed for
25 the ZAF. Also, to improve the productivity, a very short bonding time and low bonding temperature such as 180°C for 20 seconds are required. Moreover, with the progress of circuits, the alignment has become more difficult and the number of connection failures has also increased. So
30 repairability is essential; repairability is defined as the ease by which the substrate is cleaned with normal solvents.

As disclosed in JPP1987-181379 and JPP1988-86781
(A), styrene-butadiene-styrene block copolymers (SBS) and
35 styrene-ethylene-butylene-styrene clock copolymers (SEBS) are used. These thermoplastic resins have good repairability, but poor heat and humidity resistance. Further, the resins are high molecular weight, and have a high melt viscosity. The resistance stability tends to

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become worse and there is a limitation in that comparatively large size conductive particles are required.

Epoxy thermoset adhesives have also been proposed; however, they are not repairable. Further, the curing speed is short, the shelf life is short, and the mixing of resin and hardeners are sometimes ineffective.

Z-axis films using cyanate films exhibit fast curing, good heat resistance, excellent resistance stability and repairability. However, cyanate esters may also easily absorb moisture, and the peel adhesion may decrease after humidity aging.

Combinations of cyanate esters and epoxy resins are disclosed in U.S. Patent No. 3,562,214. However, the addition of epoxy resins to cyanate esters remarkably decreases the heat resistance temperature. Also film-formability is significantly impaired.

It has now been discovered that certain combination of an epoxy, a cyanate ester, and a film-formable thermoplastic resin provide a z-axis film with a rapid curing speed, good heat resistance, good humidity resistance, long shelf life and excellent repairability.

Summary of the Invention

The present invention provides a composition for the formation of an anisotropically conductive adhesive film which provides good adhesive properties, excellent repairability, and good heat resistance.

Anisotropically conductive adhesives of the invention comprise:

- (a) an adhesive composition comprising about 100 parts cyanate, from 0.01 to about 10 parts catalyst, from 10 to about 300 parts film formable thermoplastic resin and from about 10 to about 500 parts epoxy resin; and
- (2) from about 0.1 to about 20 parts conductive particles per 100 parts total weight of the adhesive composition.

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The present invention further provides an anisotropic film formed from the composition.

As used herein, the terms "Z-axis film" and "ZAF" are used interchangeably to mean an adhesive film having
5 conductivity in the direction of the "Z" axis.

Detailed Description of the Invention

Compositions of the invention contain cyanate esters as major components. These resins have good heat and
10 humidity resistance and are capable of rapid curing with certain self-crosslinking catalysts.

Cyanate ester resins comprise cyanate ester compounds (monomers and oligomer) each having two or more -OCN functional groups, and typically having a cyanate
15 equivalent weight of from about 50 to about 500, preferably from about 50 to about 250. The molecular weight of the monomers and oligomers are typically from about 150 to about 2000. If the molecular weight is too low, the cyanate ester has a crystalline structure which
20 is difficult to dissolve in solvent. If the molecular weight is too high, the compatibility of the cyanate ester with other resins is poor.

Preferred compositions of the invention include one or more cyanate esters according to Formulas I, II, III
25 or IV. Formula I is represented by



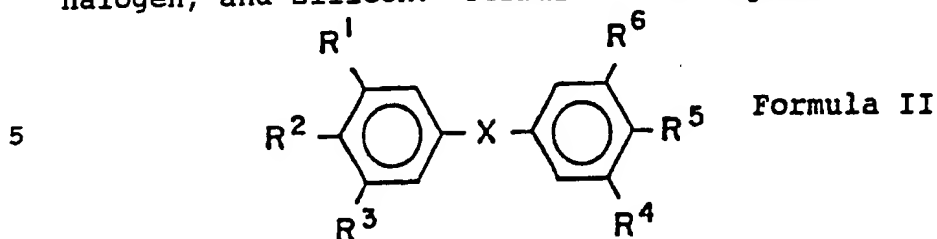
Formula I

wherein p can be from 2 to 7, and wherein Q comprises at
30 least one of the following categories: (1) a mono-, di-, tri-, or tetra-substituted aromatic hydrocarbon containing from about 5 to about 30 carbon atoms, (2) a 1 to 5 aliphatic or polycyclic aliphatic mono-, di-, tri- or tetra- substituted hydrocarbon containing from about 7
35 to about 20 carbon atoms. Optionally, either category may contain from about 1 to about 10 heteroatoms selected from the group consisting of non-peroxidic oxygen,

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sulfur, non-phosphino phosphorous, non-amino nitrogen, halogen, and silicon. Formula II is represented by



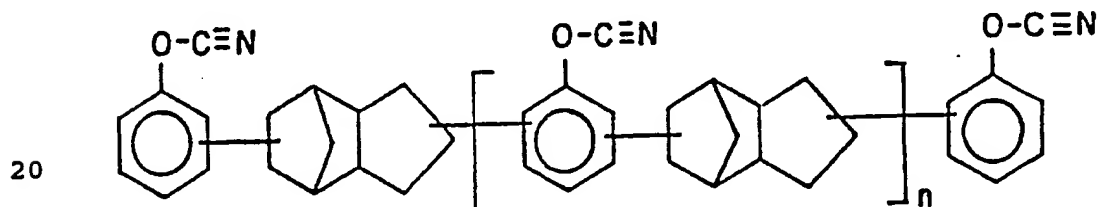
where X is a single bond, a lower alkylene group having from 1 to 4 carbons, -S-, or the SO₂ group; and where R¹, R², R³, R⁴, R⁵, and R⁶ are independently hydrogen, an alkyl group having from one to three carbon atoms, or the cyanate ester group (-OC≡N), with the proviso that at least two of R¹, R², R³, R⁴, R⁵, and R⁶ are cyanate ester groups. In preferred compounds, each of the R groups is

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Formula III is represented by

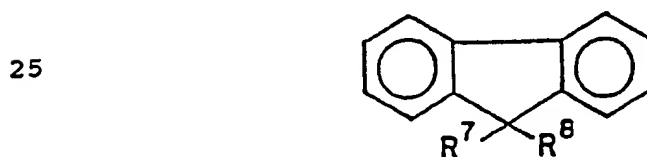
Formula III



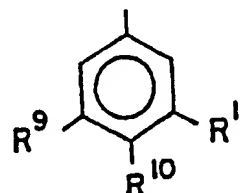
where n is from 0 to about 5.

Formula IV is represented by

Formula IV



wherein R⁷ and R⁸ are independently



wherein R⁹, R¹⁰, R¹¹ are independently -H, a lower alkyl group having from about 1 to about 5 carbon atoms, or the cyanate ester group, preferably hydrogen, methyl or the cyanate ester group, with the proviso that R⁷, and R⁸ combined include at least two cyanate ester groups.

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Useful cyanate ester compounds include, but are not limited to the following:

- 1,3- and 1,4-dicyanobenzene;
- 2-tert-butyl-1,4-dicyanobenzene;
- 5 2,4-dimethyl-1,3-dicyanobenzene;
- 2,5-di-tert-butyl-1,4-dicyanobenzene;
- tetramethyl-1,4-dicyanobenzene;
- 4-chloro-1,3-dicyanobenzene;
- 1,3,5-tricyanobenzene;
- 10 2,2'- and 4,4'-dicyanobiphenyl;
- 3,3',5,5'-tetramethyl-4,4'-dicyanobiphenyl;
- 1,3-, 1,4-, 1,5-, 1,6-, 1,8-, 2,6-, and 2,7-dicyanonaphthalene;
- 1,3,6-tricyanonaphthalene;
- 15 bis(4-cyanophenyl)methane;
- bis(3-chloro-4-cyanophenyl)methane;
- bis(3,5-dimethyl-4-cyanophenyl)methane;
- 1,1-bis(4-cyanophenyl)ethane;
- 2,2-bis(4-cyanophenyl)propane;
- 20 2,2-bis(3,3-dibromo-4-cyanophenyl)propane;
- 2,2-bis(4-cyanophenyl)-1,1,1,3,3,3-hexafluoropropane;
- bis(4-cyanophenyl)ester;
- bis(4-cyanophenoxy)benzene;
- bis(4-cyanophenyl)ketone;
- 25 bis(4-cyanophenyl)thioether;
- bis(4-cyanophenyl)sulfone;
- tris(4-cyanophenyl)phosphate, and
- tris(4-cyanophenyl)phosphate.

- Also useful are cyanic acid esters derived from
- 30 phenolic resins, e.g., as disclosed in U.S. Patent 3,963,184, cyanated novolac resins derived from novolac, e.g., as disclosed in U.S. Patent No. 4,022,755, cyanated bis-phenol-type polycarbonate oligomers derived from bisphenol-type polycarbonate oligomers, as disclosed in
 - 35 U.S. Patent 4,096,913, cyano-terminated polyarylene ethers as disclosed in U.S. Patent No. 3,595,000, and dicyanate esters free of ortho hydrogen atoms as

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disclosed in U.S. Patent No. 4,740,584, mixtures of di- and tricyanates as disclosed in U.S. Patent No.

4,709,008, polyaromatic cyanates containing polycyclic aliphatic groups as disclosed in U.S. Patent No.

5 4,528,266, e.g., QUARTEX™ 7187, available from Dow Chemical, fluorocarbon cyanates as disclosed in U.S. Patent No. 3,733,349, and cyanates disclosed in U.S. Patents 4,195,132, and 4,116,946, all of the foregoing patents being incorporated by reference.

10 Polycyanate compounds obtained by reacting a phenol-formaldehyde precondensate with a halogenated cyanide are also useful.

Examples of preferred cyanate ester compositions include low molecular weight oligomers, e.g., from about
15 250 to about 1200, of bisphenol-A dicyanates such as AroCy UC-30 Cyanate Ester Semisolid Resin, commercially available from Hi-Tex polymers, Jeffersontown, Kentucky; low molecular weight oligomers of tetra o-methyl
bisphenol F dicyanates, such as AroCy M-30 Cyanate Ester
20 Semisolid Resin, also commercially available from Hi-Tek Polymers; low molecular weight oligomers of thiodiphenol dicyanated, such as AroCy T-30 Cy.

Known curing catalysts are useful in compositions of the invention. An organometallic compound, metal chelate
25 or an organometallic salt are suitable candidates. An organometallic is defined as a compound which has at least one carbon directly connected to a metal atom. Metal chelate compounds are defined as those compounds having a ligand over 1-6 and such catalysts as
30 acetylacetonate copper. These catalysts are activated by both heat and light, and therefore exposure to heat can shorten the curing time even more. They are easily dissolved and dispersed in the adhesive solution.

Catalysts for the reaction of the cyanate ester
35 include organometallic compounds containing a cyclopentadienyl group, C_5H_5 , and suitable derivatives, such as cyclopentadienyl iron dicarbonyl dimer,

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[C₅H₅Fe(CO)₂]₂, pentamethylcyclopentadienyl iron dicarbonyl dimer, [C₅(CH₃)₅Fe(CO)₂], methylcyclopentadienyl manganesetricarbonyl, all available from Strem Chemical Company, Newburyport, Massachusetts, and

5 hexafluorophosphate salt of the cyclopentadienyl iron mesitylene cation, C₅H₅ (mesitylene)Fe⁺PF₆⁻, and trifluoromethanesulfonate salt of the cyclopentadienyl iron mesitylene cation, C₅H₅ (mesitylene)Fe⁺CF₃SO₃⁻, both of which may be prepared as described in U.S. Patent

10 4,868,277, incorporated herein by reference.

Other organometallic compounds which are suitable catalysts for use in the present invention are disclosed in EPO Publication No. 364,073. Suitable sources of radiation for photoactivation of the catalysts include

15 such conventional sources as mercury vapor discharge lamps, tungston lamps, xenon lamps, fluorescent lamps, sunlamps, lasers, carbon arcs, and sunlight. Photoactivated catalysts are preferred as they increase shelf life.

20 Useful film-formable thermoplastics are those having good compatibility with cyanate ester and a group reactive to epoxy. Included in this class are polyvinylbutyral, polyvinylformyl, polyvinylacetal, polyamide, phenoxy, polysulfone, polycarbonate siloxane,

25 polyvinyl, epoxy acrylate, glycidyl acrylate, carboxylated SEBS, epoxylated SEBS and the like. Preferred thermoplastics are those having molecular weights between about 3,000 and about 200,000. If the molecular weight is below about 3000, the resin has a

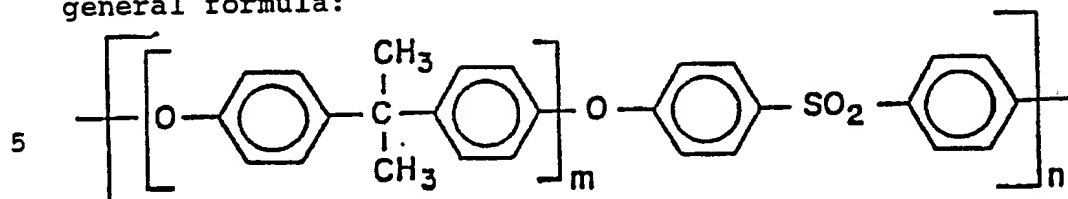
30 poor film-forming ability; if the molecular weight is over 200,000, the thermoplastic and the cyanate ester will not mix adequately, and the curing time is significantly extended.

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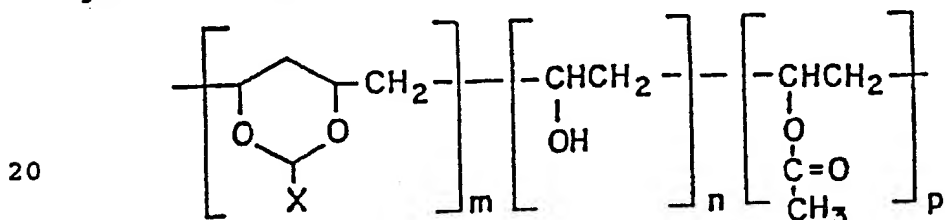
Suitable polysulfones include those having the general formula:



wherein m is 0 or 1, and n is 10 to 500. When m is 0, n is preferably from about 12 to about 50, and when m is 1, n is preferably from about 40 to about 70.

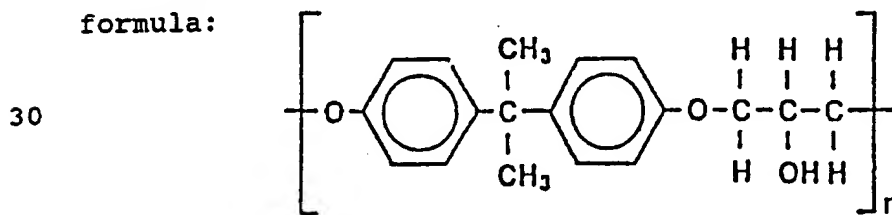
10 Examples of suitable polysulfones include "P1700-NT11", commercially available from Amoco Performance Products, Ridgefield, CT; and "Vitrex PES 5003P", commercially available from ICI Advanced materials, Wilmington, DE.

15 Suitable polyvinyl acetals are those having the general formula:



wherein X is -H or a C₁-C₄ alkyl group, and m is from about 80 to about 2400, n is from about 10 to about 2200, and p is from 0 to about 500. Preferably, m is greater than n, n is greater than p, m is less than 800, and each monomer is randomly distributed.

Suitable phenoxy resins have the following general formula:



wherein n is 75 to 150.

Useful phenoxy resins include "UCAR" resins, available in three molecular weight grades ranging from 25,000 to 35,000, from Union Carbide Company, Danbury, CT.

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Examples of useful polyvinylacetals include polyvinylbutyals, such as Sekisui S-LEC BX-L.

Examples of useful polyamides include Unires 2636, commercially available from Union Camp, Jacksonville, FL.

5 Examples of polyesters include Dynapol 206, commercially available from HULS America, Inc. One useful polycarbonatesiloxane is LR3320, from General Electric, Schenectady, NY. Examples of polyvinyls include polystyrene, polyacrylates, and
10 polymethacrylates.

An epoxy resin is defined as a resin having more than one epoxy group. Preferably, conventional epoxy resins having from about 150 to about 400 epoxy equivalents may be used. The epoxy resin comprises from
15 about 10 to about 500 parts by weight per 100 parts of cyanate ester. If the epoxy content is below 10 parts, the heat and humidity resistance is only slightly improved. If the content is over 500 parts by weight, there is unreacted epoxy resin left and initial peel
20 adhesion decreases.

Known conductive materials can be chosen from such as metal particles, coagulated metal particles, solder particles, and conductive particles having a polymer core thin metal surface layer. Compositions of the invention
25 contain from about 0.1 part to about 20 parts by weight of the conductive material to 100 parts by total adhesive weight. If the conductive material content is below 0.1 part, resistance stability decreases. If the content is above 20 parts, there is a high possibility of short
30 circuit.

The invention can further comprise other thermosetting resins such as phenolic and silicone resins, epoxy hardeners, tackifiers, coupling agents, antioxidants, modifiers and additives without departing
35 from the spirit of the invention.

All percents, parts and ratios herein are by weight unless specifically stated otherwise. The following

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examples are meant to be illustrative and do not limit the scope of the invention, which is defined solely by the claims.

5

EXAMPLESEXAMPLE 1(1) Preparation of the adhesive

100 g of "Arocy B10" (2,2-bis(4-cyanophenyl) propane), having a molecular weight (Mw) of 270, available from Hi-Tek, was used as the cyanate ester and 100 g of "Eslec BX-1" a polyvinyl-butyril (PVB), having a Mw of 100,000, available from Sekisui Chemical was used as a film-formable thermoplastic resin. They were dissolved into 200 g of MEK, "Quatrex 1010", a DGEBA type epoxy with an epoxy equivalent weight of 186, available from Dow Chemical Co.), along with 0.5 g of cyclopentadienyl-Fe-dicarbonyl dimer $((C_5H_5.Fe(CO)_2)_2$ /iron dicarbonyl/dimer (ICD) as a curing catalyst and 15 g of Finepearl™ Au-10s (Au plated polymer particle, average dia. 10 μ , Sumitomo chem.) were added to the solution. The solution was then applied on a releasing polyester film (thickness 50 μ) with a hand applicator and dried in the oven.

Thus the ZAF with a thickness of 23 μ was obtained.

25 (2) Resistance and peel adhesion test

Commercial gold (Au) plated Copper/polymide film printed circuit (pitch=0.2 mm, conductor width=0.1mm) (FPC) and ITO glass (arc resistivity=30 ohm/sq) was bonded at 180°C and 30Kg/cm² pressure for 20 seconds. Resistance and peel adhesion were measured respectively by a multimeter and a tensiometer before and after humidity aging for 250 hours at 85°C and 85% RH.

30 (3) Short circuit

The above FPC and an insulative glass were bonded at 180°C and 30Kg/cm² pressure for 20 seconds. The insulative resistance between 200 adjacent conductors was measured by a multimeter.

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(4) TGA

The ZAF was cured at 180°C for 30 minutes in the oven. After that, 5 wt% weight loss temperature was measured by TGA951 (Dupont).

5 (5) Tg

Tg was measured by DSC4 (Perkin Elmer).

(6) Curing speed 1

Curing speed was estimated from DSC peak temperature.

10 (7) Curing speed 2

Curing speed was estimated from tack free time (TFT) by a plate gelling timer. TFT is the time until there is no remaining tack on the surface of the sample.

(8) Shelf life

15 Shelf life was studied from the viewpoint of flexibility of the ZAF film, and is defined as the time until a crack is produced when the film is bent at 180°.

(9) Repairability

20 An FPC and an ITO glass were bonded at 180°C for 30Kg/cm² pressure for 20 seconds. After peeling off the FPC, the time until the adhesive residue was cleaned with acetone was measured.

EXAMPLES 2 TO 14

25 In examples 2-14, various types and amounts of cyanate esters, catalysts, and epoxy resins were tested. The preparation of the ZAF and the measurement method were the same as Example 1. The resins used were as follows:

30 Cyanate Ester Resin

AROCY B10 (2,2-bis(4-cyanophenyl)propane, Mw=270, Hi-Tek)
AROCY B30 (2,2-bis(4-cyanophenyl)propane, Mw=560, Hi-Tek)
AROCY B50 (2,2-bis(4-cyanophenyl)propane, Mw=1100, Hi-Tek)

35 AROCY M30 bis(3,5-dimethyl)(4-cyanophenyl)methane,
Mw=490, Hi-Tek)

QUATREX XU71787 (cycloaliphatic cyanate ester, Dow chem.)

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Catalyst

Co naphthenate, Cu naphthenate, Cu acetylacetonate,
Mn₂(co) 10, IDC

5 Thermoplastic

- UCAR PKHC (phenoxy, Mw=25000, UCC)
UCAR PKHH (PVB, Mw=35000, UCC)
ESLEC BX-5 (PVB, Mw=150000, Sekisui chem.)
ESLEC BXL (PVB, Mw=18000, Sekisui chem.)
10 FORMVAR 7/95s (polyvinylformaar, Mw=18000, Monsanto)
TAFUTEC M1913 (calboxylated SEBS, Mw=50000, Asahi chem.)

Epoxy resin

- QUATREX1010 (DGEBA type epoxy, EEW=186, Dow chem.)
EPIKOTE 152 (Novolac liquid epoxy, EEW=175, Shell
15 Chemical Co.)
EPOTOHTO YR102 (rubber modified epoxy, EEW=1200, Tokyo
Chemical Co.)
ERL 4221 (cycloaliphatic epoxy, EEW=137, UCC)

Conductive Material

- 20 Finepearl Au10s (Au plated polymer particle, Ave.
diameter 10 μ , Sumitomo Chemical Co.)
T123 (Carbon Ni, Ave. dia. 4 μ , Inco)
SF-PbSn6040 (Superfine solder powder, Ave. dia. 10 μ ,
Nippon Atomize)
25 The results are shown in Table 1. The resins used in
Examples 1 through 14 are as follows:

| | EX. | CYANATE | CATALYST | THERMO PLASTICS | EPOXY | PARTICLE |
|----|-----|---------|----------------------------|--------------------|------------|----------|
| | 1 | B10/100 | IDC/1.0 | BX1/100 | 1010/100 | AU10s/15 |
| 30 | 2 | B30/100 | IDC/0.1 | BXL/50 | 1010/10 | AU10S/8 |
| | 3 | B30/100 | IDC/3.0 | BXL/200 | 1010/30 | AU10s/9 |
| | 4 | B30/100 | IDC/5.0 | BXL/300 | 1010/50 | AU10s/15 |
| | 5 | B10/100 | IDC/1.0 | BX1/100 | 152/300 | AU10S/50 |
| | 6 | B10/100 | IDC/1.0 | BX1/100 | 152/500 | AU10s/9 |
| 35 | 7 | B50/100 | IDC/0.01 | PKHC/50 | YR102/100 | AU10s/15 |
| | 8 | B10/100 | AcAcCu/0.5 | M1913/20 | YR102/30 | AU10S/8 |
| | 9 | XU/100 | AcAcCu/10 | 7/95S/30 | YR102/200 | AU10s/9 |
| | 10 | XU/100 | Mn ₂ (CO)10/2.C | BX5/10 | ERL4221/50 | AU10s/15 |
| | 11 | XU/100 | CoNp/1.0 | PKHH/50 | ERL4221/75 | AU10S/8 |
| 40 | 12 | B10/100 | CuNp/1.0 | BXL/150 | 1010/10 | AU10s/9 |
| | 13 | B10/100 | IDC/3.01 | BX1/200 | 1010/50 | AU10S/8 |
| | 14 | B50/100 | IDC/3.0 | PKHH/100 | 152/100 | AU10s/9 |

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TABLE 1

| EX | INITIAL RESIST. | AGED RESIST. | INITIAL ADHESION | AGED ADHESION | SHORT CIRCUIT | TGA | DSC T _g | DSC PEAK TEMP | TFT | SHELF LIFE | REPAIR. |
|----|--------------------|-----------------|---------------------|------------------|---------------------------------------|---------|-----------------------|------------------|-----------|---------------|-----------|
| 1 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 2 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 700 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 300°C | ≥ 80°C | ≤ 170°C | ≤ 30 sec. | ≥ 2 weeks | ≤ 30 sec. |
| 3 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 4 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 5 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 250°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 6 | ≤ 100 Ohm | ≤ 100 Ohm | ≥ 700 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 250°C | ≥ 80°C | ≤ 170°C | ≤ 30 sec. | ≥ 2 weeks | ≤ 10 sec. |
| 7 | ≤ 100 Ohm | ≤ 100 Ohm | ≥ 700 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 30 sec. | ≥ 2 weeks | ≤ 10 sec. |
| 8 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 9 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 10 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |
| 11 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁶ Ohm | ≥ 300°C | ≥ 100°C | ≤ 170°C | ≤ 30 sec. | ≥ 1 month | ≤ 10 sec. |
| 12 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 80°C | ≤ 170°C | ≤ 30 sec. | ≥ 2 weeks | ≤ 30 sec. |
| 13 | ≤ 100 Ohm | ≤ 100 Ohm | ≥ 700 g/cm | ≥ 700 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 170°C | ≤ 30 sec. | ≥ 2 weeks | ≤ 30 sec. |
| 14 | ≤ 50 Ohm | ≤ 50 Ohm | ≥ 1000 g/cm | ≥ 1000 g/cm | 0 resistance ≥ 10 ⁸ Ohm | ≥ 300°C | ≥ 100°C | ≤ 150°C | ≤ 10 sec. | ≥ 1 month | ≤ 10 sec. |

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COMPARATIVE EXAMPLES 1-6

These Comparative Examples are examples outside the scope of this invention. Comparative Example 5 is an example using G1650 (SEBS, Shell Chem.) a thermoplastic resin which does not have a reactive group for an epoxy resin. The test results are shown in Table 2. The resins used in comparative examples 1 through 6 are as follows:

| EX. | CYANATE | CATALYST | THERMO PLASTICS | EPOXY | PARTICLE |
|-----|---------|-----------|--------------------|----------|------------|
| 10 | | | | | |
| 1 | 310/100 | IDC/0.005 | BX1/400 | 0 | AU10s/2.5 |
| 2 | B30/100 | IDC/20 | BXL/5 | 152/50 | AU10s/1.0 |
| 3 | B30/100 | IDC/1.0 | PKHC/100 | 1010/800 | T123/10.0 |
| 15 | 4 | XU/100 | AcAcCu/1 | PKHC/50 | 1010/300 |
| 5 | XU/100 | AcAcCo/15 | BXL/50 | 152/5 | T123/0.1 |
| 6 | XU/100 | IDC/5 | G165C/300 | 152/10 | AU10s/10.0 |

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TABLE 2

| EX | INITIAL RESIST. | AGED RESIST. | INITIAL ADHESION g/cm | AGED ADHESION g/cm | SHORT CIRCUIT | TGA | DSC T _g | DSC PEAK TEMP | TFT | SHELF LIFE | REPAIR. |
|----|--------------------|-----------------|-----------------------------|--------------------------|---------------------------------------|--------|-----------------------|------------------|----------|---------------|----------|
| 1 | ≤500 Ohm | ≤500 Ohm | ≥ 500 g/cm | ≥ 500 g/cm | 0 resistance ≥10 ⁶ Ohm | <200°C | < 60°C | >190°C | >60 sec. | <1 week | ≤30 sec. |
| 2 | ≤ 50 Ohm | ≤500 Ohm | ≥1000 g/cm | ≥1000 g/cm | 0 resistance ≥10 ⁶ Ohm | ≥200°C | ≥ 60°C | ≤150°C | ≤10 sec. | <1 week | ≤60 sec. |
| 3 | >500 Ohm | >500 Ohm | ≥ 500 g/cm | ≥ 500 g/cm | 0 resistance ≥10 ⁶ Ohm | <200°C | < 60°C | ≤190°C | ≤60 sec. | ≥1 week | ≤10 sec. |
| 4 | ≤ 50 Ohm | ≤ 50 Ohm | ≥1000 g/cm | ≥1000 g/cm | ≥1 resistance <10 ⁶ Ohm | ≥300°C | ≥100°C | ≤150°C | ≤10 sec. | ≥1 month | ≤10 sec. |
| 5 | ≤500 Ohm | ≤500 Ohm | ≥ 500 g/cm | > 500 g/cm | 0 resistance ≥10 ⁶ Ohm | ≥250°C | ≥ 80°C | ≤150°C | ≤10 sec. | ≥1 month | >60 sec. |
| 6 | >500 Ohm | >500 Ohm | > 500 g/cm | > 500 g/cm | 0 resistance ≥10 ⁶ Ohm | <200°C | < 60°C | >190°C | >60 sec. | ≥1 month | ≤10 sec. |

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What is Claimed is:

1. An anisotropically conductive adhesive comprising:

5 (a) an adhesive composition comprising about 100 parts of cyanate ester, from about 0.01 to about 10 parts of a catalyst, from about 10 to about 300 parts of a film formable thermoplastic resin, and from about 10 to about 500 parts of an epoxy resin; and

10 (b) from about 0.1 to about 20 parts conductive particles per 100 parts total weight of said adhesive.

2. The anisotropically conductive adhesive of claim 1, wherein said catalyst is selected from the group consisting of organometallic compounds, metal chelates
15 and organometallic salts.

3. The adhesive of claim 1 wherein said film formable thermoplastic resin is selected from the group consisting of polyvinylbutyral, polyvinylformal,
20 polyvinylacetal, polyamide, phenoxy, polysulfone, polyacrylate, glycidyl acrylate, styrene-butadiene-styrene block copolymers, carboxylic styrene-ethylene-butylene-styrene block copolymers, and epoxylic styrene-ethylene-butylene-styrene block copolymers.

25 4. The adhesive of claim 3 wherein the film formable thermoplastic resin has a molecular weight of from about 3,000 to about 200,000.

30 5. The adhesive of claim 1 wherein the cyanate ester is selected from the group consisting of: 2,2-bis(4-cyanophenyl)propane, 2,2-bis(4-cyanophenyl)propane, 2,2-bis(4-cyanophenyl)propane, bis(3,5-dimethyl)(4-cyanophenyl)methane, and
35 cycloaliphatic cyanate ester.

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6. The anisotropically conductive adhesive of claim 1 wherein said conductive particles are selected from the group consisting of metal particles, coagulated metal particles, solder particles, and conductive
5 particles having a polymer core and a thin metal surface layer.

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INTERNATIONAL SEARCH REPORT

PCT/US 92/04411

International Application No

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| Int.Cl. 5 | C09J163/00; | C08G73/06; H01B1/22; C08G59/40 |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.Cl. 5 | C09J ; H01B ; C08G | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| Y | DE,A,3 423 385 (MITSUBISHI GAS CHEMICAL CO.) 10 January 1985 see example 6; table 1 see page 8, line 34 - page 9, line 2 see page 4, line 34 - line 37 see page 6, line 10 - line 13 see page 7, line 36 - page 8, line 5 see page 9, line 33 - line 35 --- | 1-3,5,6 |
| Y | EP,A,0 242 025 (HITACHI CHEMICAL CO.) 21 October 1987 see claim 1 see page 6, line 47 - line 52 --- | 1-3,5,6 |
| A | EP,A,0 266 986 (AMOCO CORPORATION) 11 May 1988 see claim 1 see page 4, line 7 see page 4, line 4 - line 5 --- | 1,3,5 |
| <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report | |
| 18 SEPTEMBER 1992 | 29. 09. 92 | |
| International Searching Authority | Signature of Authorized Officer | |
| EUROPEAN PATENT OFFICE | O'SULLIVAN T.P. | |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9204411
SA 61026

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 18/09/92

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